REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
10-06-2015	Final	28 Mar 13 – 27 Mar 15

4. TITLE AND SUBTITLE
Development of Sesquioxide Ceramic for High Energy Lasers

5a. CONTRACT NUMBER FA2386-13-1-4097
5b. GRANT NUMBER Grant AOARD-134097
5c. PROGRAM ELEMENT NUMBER 61102F
5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

6. AUTHOR(S)
Dr. Akio Ikesue

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
World Labo Co., Ltd.
1-2-19-CSJ308 , Mutsuno, Atsuta-ku
Nagoya 456-0023
Japan

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR/IOA(AOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-134097

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Code A: Approved for public release, distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
In this project, the PI was able to evaluate the performance of developed materials with new standards and evaluation methods. Simultaneously, he was able to extract the unique problem of sesquioxide materials and improve their quality. The significance of the findings include, the relationship between the appropriate evaluation process for the performance of materials and laser oscillation performance. The following findings were obtained from this project.
1) Fabrication of highly transparent (theoretical transmittance) rare-earth oxide ceramics was successful.
2) In-line transmittance and optical homogeneity of host materials such as Sc2O3, Lu2O3 and Y2O3 ceramics were excellent.
3) Optical homogeneity was lowered by adding laser active ions into the above host materials.
4) Optical heterogeneity was caused by the inhomogeneous distribution of laser active ions in the host materials.
5) Due to the phenomenon described in 4), laser oscillation efficiency gets lower or in the worst case, laser oscillation is not possible. (However, when the laser gain length is extremely reduced, both laser output power and laser oscillation efficiency can be significantly improved.)
6) Even for ceramic materials derived from co-precipitated powders, improved performance was not recognized (as of this current project).
7) Production of large scaled laser gain media by ceramic process is available.
What new research questions came about from this project:
The outstanding issue is the formation of optically inhomogeneous parts when laser ions are doped into the host materials. The following investigations are required to resolve the above mentioned technical issue.
1) Development of chemically homogeneous co-precipitated powders with good sinterability and optimization of sintering process for those starting materials.
2) Development of mixing process in solid-state method that can provide homogeneous dispersion of laser active ions in the host materials and optimization of sintering process for those starting materials.
In conclusion, “whether the development of laser materials is successful or not” is finally reflected by the laser oscillation results but before that, verification on material science is more important.

15. SUBJECT TERMS
Laser Materials Processing, Ceramic Matrix Composites, Ceramics

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Kristopher, Ahlers, Lt Col, USAF, Ph.D.
U	U	U	SAR	21	**19b. TELEPHONE NUMBER** *(Include area code)* +81-42-511-2000

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **10 JUN 2015**	2. REPORT TYPE **Final**	3. DATES COVERED **28-03-2013 to 27-03-2015**
4. TITLE AND SUBTITLE **Development of Sesquioxide Ceramic for High Energy Lasers**		5a. CONTRACT NUMBER **FA2386-13-1-4097**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER **61102F**
6. AUTHOR(S) **Akio Ikesue**		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **World Labo Co., Ltd.,1-2-19-CSJ308 , Mutsuno, Atsuta-ku,Nagoya 456-0023,Japan,NA,NA**		8. PERFORMING ORGANIZATION REPORT NUMBER **N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96338-5002**		10. SPONSOR/MONITOR’S ACRONYM(S) **AFRL/AFOSR/IOA(AOARD)**
		11. SPONSOR/MONITOR’S REPORT NUMBER(S) **AOARD-134097**
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		

14. ABSTRACT

In this project, the PI was able to evaluate the performance of developed materials with new standards and evaluation methods. Simultaneously, he was able to extract the unique problem of sesquioxide materials and improve their quality. The significance of the findings include, the relationship between the appropriate evaluation process for the performance of materials and laser oscillation performance. The following findings were obtained from this project. 1) Fabrication of highly transparent (theoretical transmittance) rare-earth oxide ceramics was successful. 2) In-line transmittance and optical homogeneity of host materials such as Sc2O3, Lu2O3 and Y2O3 ceramics were excellent. 3) Optical homogeneity was lowered by adding laser active ions into the above host materials. 4) Optical heterogeneity was caused by the inhomogeneous distribution of laser active ions in the host materials. 5) Due to the phenomenon described in 4), laser oscillation efficiency gets lower or in the worst case, laser oscillation is not possible. (However, when the laser gain length is extremely reduced, both laser output power and laser oscillation efficiency can be significantly improved.) 6) Even for ceramic materials derived from co-precipitated powders, improved performance was not recognized (as of this current project). 7) Production of large scaled laser gain media by ceramic process is available. What new research questions came about from this project The outstanding issue is the formation of optically inhomogeneous parts when laser ions are doped into the host materials. The following investigations are required to resolve the above mentioned technical issue. 1) Development of chemically homogeneous co-precipitated powders with good sinterability and optimization of sintering process for those starting materials. 2) Development of mixing process in solid-state method that can provide homogeneous dispersion of laser active ions in the host materials and optimization of sintering process for those starting materials. In conclusion, ???whether the development of laser materials is successful or not??? is finally reflected by the laser oscillation results but before that, verification on material science is more important.

15. SUBJECT TERMS

Laser Materials Processing, Ceramic Matrix Composites, Ceramics

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**21**	

AOARD Contract no.: FA2386-13-1-4097

Final report for the project on:

“Development of Sesquioxide Ceramic for High Energy Laser”

Period of Performance: From Mar. 28th, 2013 - To Mar. 27th, 2015

Submission Date: May 25th, 2015

Principal Investigator: **Dr. Akio Ikesue**

World-Lab. Co., Ltd.

E-mail: poly-ikesue@s5.dion.ne.jp

Funding level: $130,000/year for 2 years

Grant period: Mar. 28 2013 to Mar. 27 2015

Significant publications: None

Content

Abstract

Highly transparent Nd, Yb or Er doped Sc_2O_3, Y_2O_3 and Lu_2O_3 ceramics were successfully fabricated by solid-state method and co-precipitation method. Optical scattering losses of the fabricated ceramics were extremely low in the wavelength regions of pumping and laser oscillation. SEM-EDS and HRTEM-EDS analysis results revealed that the microstructure of these ceramics can assure the fact of low optical scattering. However, slight variations of refractive index in these ceramics which can be regarded as optical domains were detected by optical microscope and Schlieren imaging system. A correlation between laser gain length and oscillation efficiency was recognized. The optical domains (optically inhomogeneous parts) are considered to be the main factor of this correlation. The only outstanding issue in this work is to remove such optical domains from the ceramics. We anticipated that this issue will become a key technology for the development of gain media for high energy lasers.

1. Introduction

Sesquioxide host materials such as Sc_2O_3, Y_2O_3, and Lu_2O_3 have recently been deemed laser material of choice for power scaling bulk solid state lasers to 100s of kW. This interest is primarily driven by sesquioxide hosts (especially Lu_2O_3) having a much higher thermal conductivity than YAG even when doped with high concentrations of rare earth such as ytterbium (Yb), neodymium (Nd), erbium (Er), thulium (Tm) and holmium (Ho). However, the melting points of the sesquioxide materials are ~2400ºC thus eliminating the conventional melt-growth process used to fabricate single laser media since the iridium crucible used in conventional melt-growth process has a melting point well below 2400ºC. In addition, the sesquioxide materials also have a phase transition point just below the melting point. On the other hand, fabrication of sesquioxides using ceramic processing is possible since ceramic processing requires 25-30% lower temperature than the melting temperature and still can lead to usable dimension with laser quality transparent sesquioxide materials. While lasing has been demonstrated in sesquioxides materials, the power level generated is very low (<25 Watts) to be of any use for most applications and there are no reports which describe or show pictures with any significant details the optical quality of the samples used, fabrication of transparent laser quality sesquioxides via ceramic processing is still in the infancy development stages. Unlike garnet materials such as YAG, sesquioxide materials are non-stoichiometric materials, and the methodology for fabricating sesquioxides needs development just as with YAG ceramic processing, optimizing the processing requires time and resources. Once the fabrication process is established, composition adjustment and sample size scaling should be relatively simple. Hence, just as with YAG, the ceramic processing of sesquioxide will lead to the development of high power and high energy lasers at relevant power levels.

Recently Yb doped and Er doped sesquioxide materials have attracted attention because Yb system has high quantum efficiency and Er system is usable for eye-safe lasers. Again, just as in the case with doping into YAG, doping Er into sesquioxide homogeneously is still a goal yet to be achieved. One of the reasons is that when Er ions are doped into Y_2O_3 or Lu_2O_3, the stable zone of cubic phase materials shifts to the lower temperature region, and as a result, the crystal lattice gets distorted or other crystal phases (non-cubic phases) may generate partially.

In this work, based on the technical issues of sesquioxide materials that have been raised, research and development on the improvement of high quality materials were performed.

2. Fabrication of materials

2-1. Fabrication by solid-state method

Fabrication process for $Yb:Y_2O_3$ ceramics by solid-state method is shown in figure 1. Particle sizes of the starting materials, Y_2O_3 and Yb_2O_3 (laser active element) were 0.1um and 0.03um, respectively. These powders were mixed by ball-milling in alcohol solvent including dispersant and a trace amount of sintering aids for 10h with ZrO_2 balls. The obtained slurry was put on a hot magnetic stirrer and the solvent was evaporated while stirring.

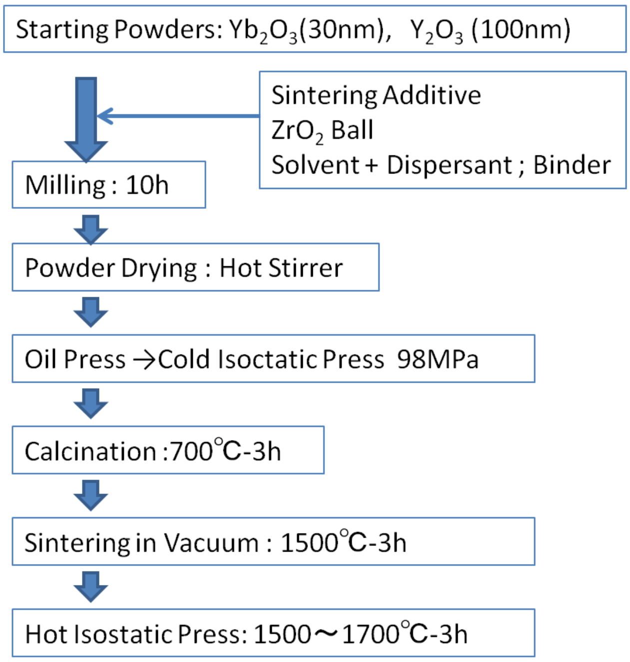


Figure 1 Fabrication flow sheet for $Yb:Y_2O_3$ ceramics by solid-state method.

The obtained powders were pressed into required shapes and sizes in metal mold by using oil-press machine, and then they were pressed again in CIP (cold isostatic press) machine at 98MPa. These powder compacts were heated at 700ºC and then pre-sintered at 1500ºC until their apparent density reached 98~99%. These sintered bodies were heat treated in HIP (hot isostatic press) machine at 1500~1700ºC. Finally, these sintered bodies got transparent after HIP treatment.

2-2. Fabrication using co-precipitated powders

Co-precipitation method was applied to prepare $Nd:Y_2O_3$, $Yb:Y_2O_3$, $Yb:Lu_2O_3$ and $Er:Y_2O_3$ starting materials. Their appearances are shown in figure 2. They were prepared by pyrolysis treatment on basic carbonic salt. As they were prepared by co-precipitation method, these starting materials have chemically homogeneous composition i.e., their composition is very close to the end composition of sintered ceramics. As same as in the above solid-state method, these co-precipitated starting powders were mixed by ball-milling in alcohol solvent including dispersant and a trace amount of sintering aids for 10h with ZrO_2 balls. The obtained slurry was put on a hot magnetic stirrer and the solvent was evaporated while stirring.

The obtained powders were pressed into required shapes and sizes in metal mold by using oil-press machine, and then they were pressed again in CIP (cold isostatic press) machine at 98MPa. These powder compacts were heated at 700ºC and then pre-sintered at 1500ºC until their apparent density reached 98~99%. These sintered bodies were heat treated in HIP (hot isostatic press) machine at 1500~1700ºC. Finally, these sintered bodies got transparent after HIP treatment.

Figure 2 Co-precipitated powders prepared for this work.
(From left to right; $Nd:Y_2O_3$, $Yb:Y_2O_3$, $Yb:Lu_2O_3$ and $Er:Y_2O_3$)

Difference of microstructure in sintered bodies between the solid-state method and co-precipitation method is illustrated in figure 3. In solid-state method, two or more different rare-earth oxides are mixed in powder condition. If there are inhomogeneous distributions of laser active powders in the mixture, the distribution of laser active ions in the sintered ceramics will become also inhomogeneous. Therefore, it is more likely that microstructure with inhomogeneous composition⇒ material composed with fine grains having different refractive indices⇒scattering interference between each fine grain ⇒ lowering laser performance (large scattering and heterogeneous fluorescence lifetime etc.).

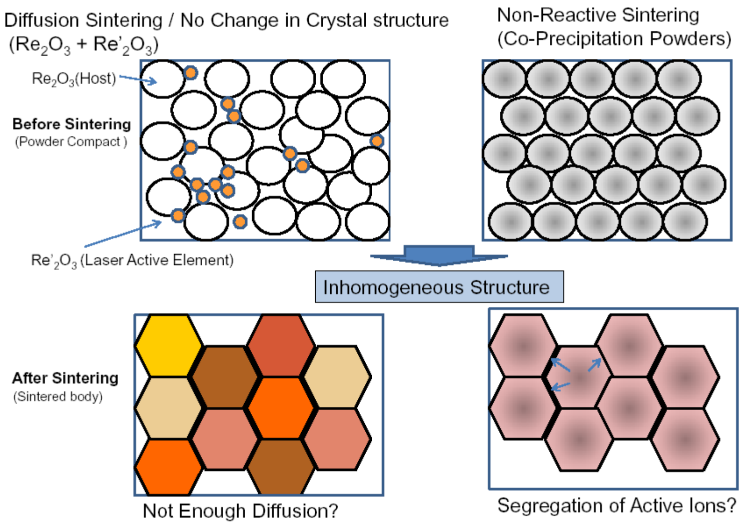


Figure 3 Illustration for difference of microstructure in sintered bodies between solid-state method (left) and co-precipitated method (right).

On the other hand, the chemical composition of the co-precipitated powders is relatively homogeneous compared to that of the solid-state powders. Therefore, it is important to figure out the technical issues (optical quality due to inhomogeneity and lowering of laser performance etc.) mentioned above can be minimized in ceramics by using the co-precipitated powders.

In the case of fabrication of sesquioxide ceramics, the crystal structure of the starting powder materials is Bixbite structure and its crystal structure does not change even after final sintering. Therefore, only volume diffusion occurs during sintering process. It is anticipated that the homogenization of chemical composition in ceramics during sintering is very difficult. As everyone knows, during laser amplification, laser light is amplified by multiple passing inside gain medium. If there are optically inhomogeneous parts (slight variation of refractive index) inside the materials, it will severely affect the laser oscillation efficiency and laser beam quality. Thus, a demanding technology to produce laser gain media is required. In this work, co-precipitation powders were introduced to solve these technical issues, but there is no guarantee that we can get an ideal material with our expected sintering mechanism by using the co-precipitated powders. In the classical solid-state method, it concerns about localization issue of ①host materials and ②laser active materials in the sintered ceramics. If there is a technique to localize ideally the ①host materials and ②laser active materials, we can expect larger mutual diffusion between raw materials with different compositions compared to using the co-precipitation powders. Therefore, it is not easy to judge in this early stage that which process is the most favorable one. Accordingly we proposed to adopt both methods (using solid-state method and using co-precipitated powders) for this work.

3. Optical properties of ceramics fabricated by solid-state method

Relationship between the measuring wavelength and refractive index of 7%Yb:Lu_2O_3 ceramics prepared in this work is shown in figure 4a. Refractive index changed depending upon the measuring wavelength. The refractive index of this ceramics at around pumping wavelengths (940, 970nm) and lasing wavelength (1030nm) was 1.913. Fresnel loss (optical loss occurred by surface scatterings) can be calculated by the following equation.

$$\text{Fresnel Loss: } \beta(\lambda)=(n(\lambda)-1)^2 / (n(\lambda)+1)^2$$

From this calculation, each surface has reflection loss of 0.098, and the theoretical transmittance can be estimated to be 80.4%. Theoretical transmittance curve calculated from the wavelength dependent of refractive index for this material is shown in figure 4b. The in-line transmittance curve for the prepared 7%Yb:Lu_2O_3 (t=7mm) ceramics is shown in figure 4c. The transmission at 1μm region is 80.3% and its optical loss is approximately 0.1~0.2%/cm, which shows low scattering.

Transmitted wavefront images by interferometry for the Yb:Lu_2O_3 ceramics developed at the beginning stage of this work and after about one year from the beginning of the development are shown in figure 5a and 5b, respectively. Although the optical loss around 1μm region is about 0.1~0.2%/cm in both samples, the optical transmission property at UV~visible wavelength regions was quite improved in the latter sample (5b). The wavefront distortion for sample (a) and (b) was λ/4 and λ/9~10, respectively.

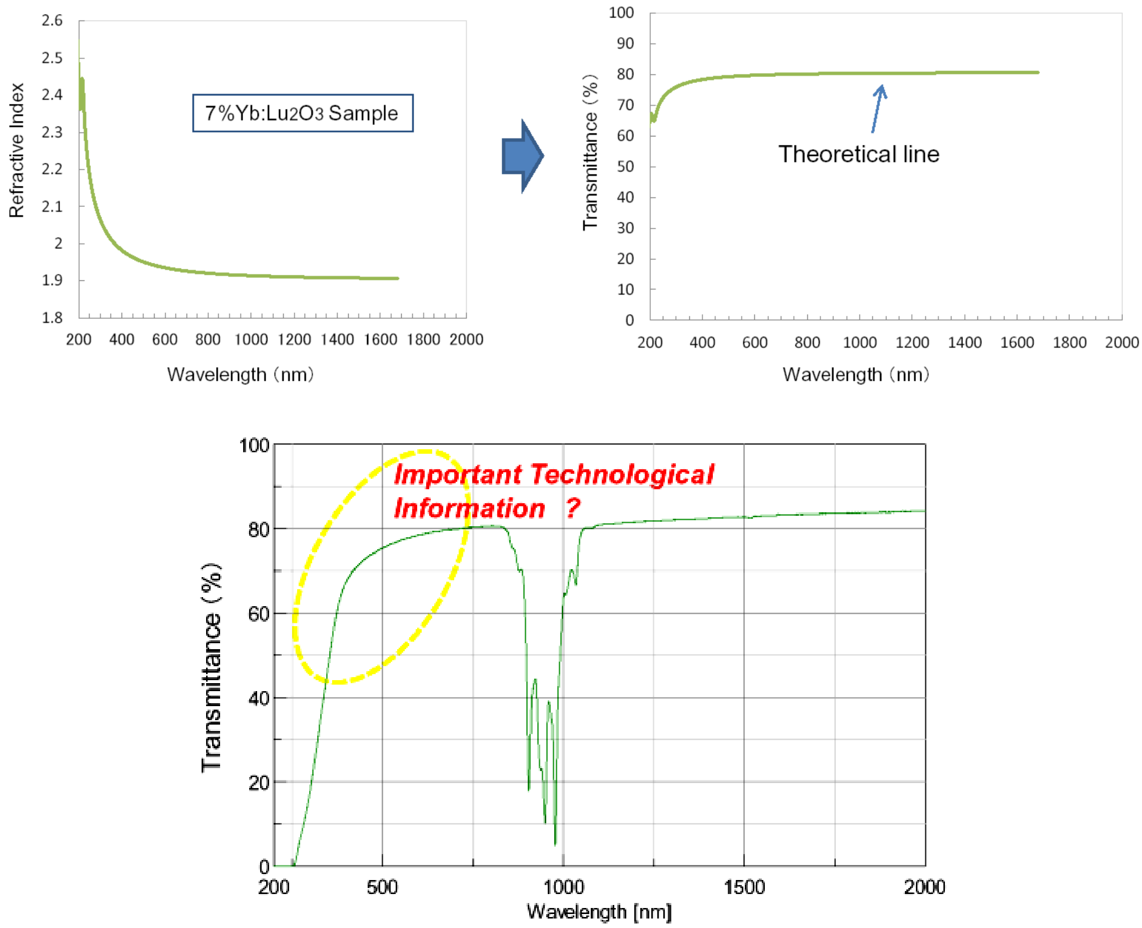


Figure 4(a) Relationship between the measuring wavelength and refractive index of 7%Yb:Lu_2O_3 ceramics. (b) Theoretical transmittance curve calculated from the wavelength dependent of refractive index. (c) In-line transmittance curve for the prepared 7%Yb:Lu_2O_3 (t=7mm) ceramics.

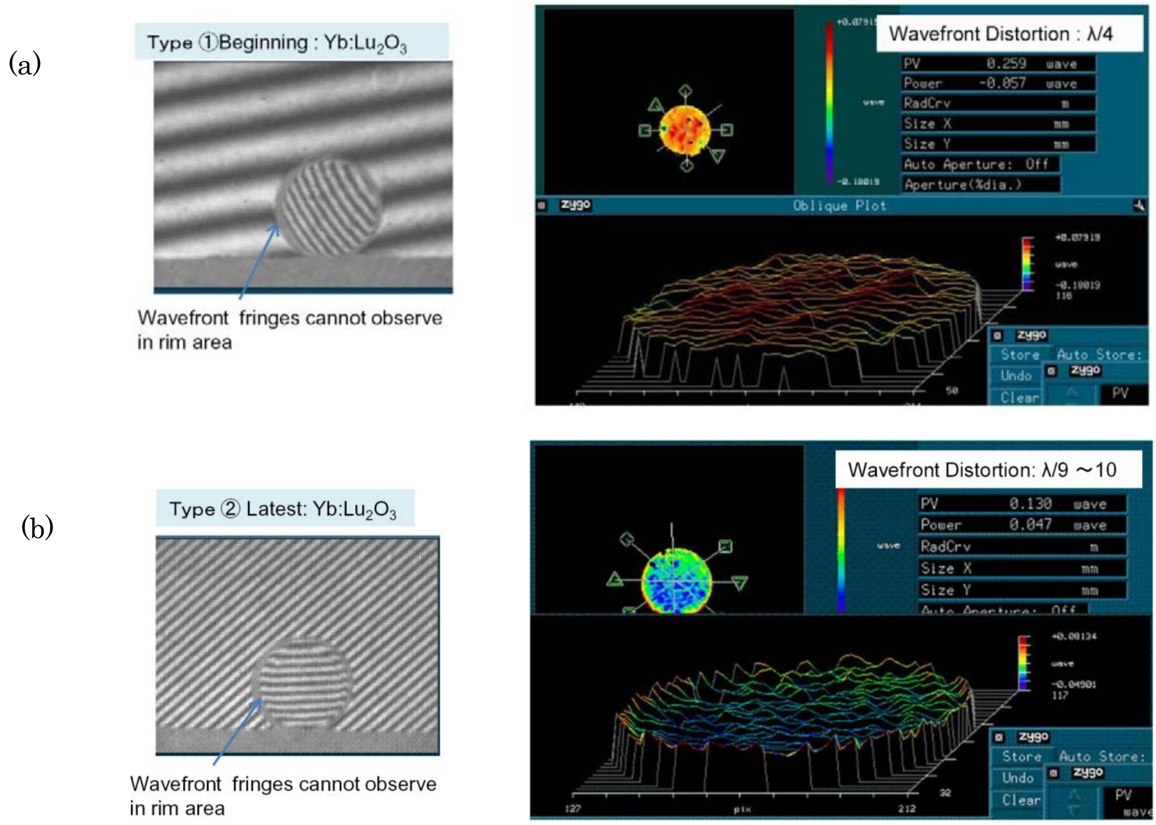


Figure 5(a) Transmitted wavefront images by interferometry for the $Yb:Lu_2O_3$ ceramics developed at the beginning stage of this work and, (b) after about one year from the beginning of the development.

In addition, ①Schlieren image, ②polarized image and ③microstructure by polarized optical microscope for the samples shown in figure 5a and 5b are summarized in figure 6. In sample (a), about sub-millimeter sized optically inhomogeneous structure was clearly observed. But in sample (b), it was observed only in localized area. By observation under polarizer, inhomogeneous double refractions were observed in sample (a), but almost nothing in sample (b). When it was observed under a polarized optical microscope, double refraction with several tens of μm domains was observed in sample (a). Similar domain structure was observed in sample (b) but it was very little. (It was possible to detect by visual observation but it seems to be difficult to be taken on photograph.) As a reference material, optical grade Yb:YAG ceramics previously prepared by the author was used to measure the Schlieren image and polarized optical microscopic image. These results are shown in figure 6b. There were no optically heterogeneous parts and the optical quality was almost ideal.

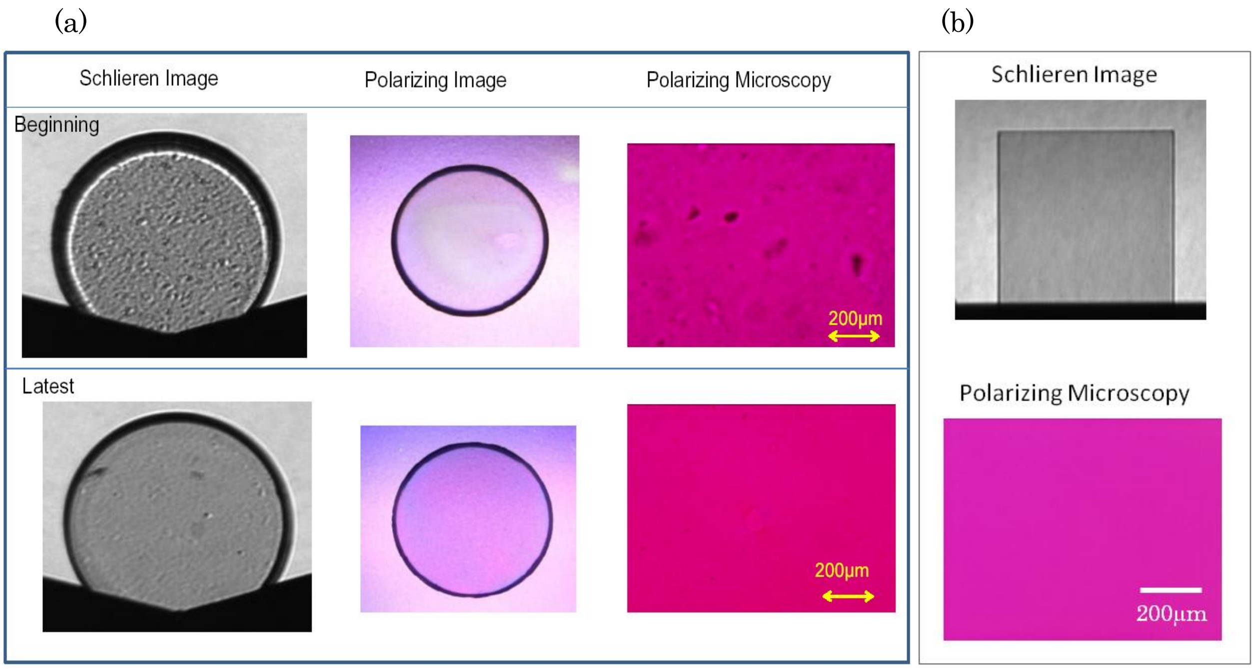


Figure 6(a) Schlieren image, polarized image and microstructure by polarized optical microscope for the samples shown in figure 5a and 5b. (b) Schlieren image and polarized microscopy for Yb:YAG.

To compare the internal optical property of transparent materials, a He-Ne laser (λ=633nm) with TEMoo (transverse electro-magnetic wave) mode was used as a light source and it was irradiated into the materials, and the transmitted laser beam pattern was recorded by using a beam profiler. As a reference, the original laser beam pattern before passing through the material is shown in figure 7a. Figure 7b is for commercial 50%Er:YAG single crystal, figure 7c is for pure Lu_2O_3 ceramics, figure 7d is for the Yb:Lu_2O_3 ceramics at the beginning stage of the development, and figure 7e is for the improved Yb:Lu_2O_3 ceramics after one year from the development. Even in the commercial single crystal, distortion in beam pattern was observed (probably one of the reason is due to very high doping of Er ions). In the case of pure Lu_2O_3 ceramics (without doping of laser active ion), beam distortion was very little, and it was better than that of the single crystal. In the case of Yb:Lu_2O_3 ceramics which was developed at the beginning of the study, optically heterogeneous parts were observed by Schlieren imaging and as seen in figure 7d, beam distortion was very bad. In the case of improved Yb:Lu_2O_3 ceramics (figure 7e) with optically homogeneous quality, it was confirmed that the beam pattern was also quite improved but compared to the original beam pattern, the distortion was recognized to some extent.

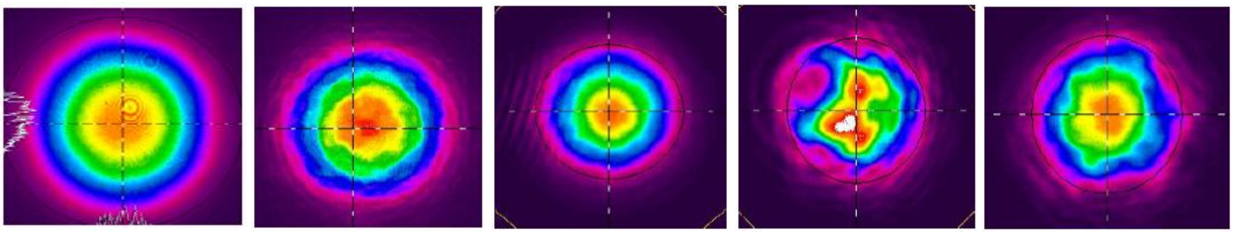


Figure 7 Inspection of optical quality by laser beam profiler (λ=633nm).

Here what we should focus on is the severe distortion of laser beam pattern caused by doping of laser active elements into the host materials. For example, Yb and Lu are neighboring elements in the periodic table and the refractive index of Yb_2O_3 and Lu_2O_3 is similar to each other. Even for a combination of these two elements, depending on the fabrication condition, an optical homogeneity was extremely poor. We can estimate that it will be very severe for the materials doped with laser active ions such as Nd and Er.

The above measurement was done by using 633nm wavelength laser source but the wavelengths for laser pumping and oscillation are around 1μm region. How about measurements by using 1μm wavelength? For this measurement, an Nd:YAG laser (λ=1064nm) with TEMoo mode was used as a light source. Figure 8a shows the original laser beam pattern before passing through the samples. Laser beam patterns after passing through the $Yb:Lu_2O_3$ ceramic samples at the beginning stage of the development and the improved quality are shown in figure 8b and 8c, respectively. Compared to figure 7d and 7e, very good beam patterns were confirmed. It is considered that the sensitivity to the optical inhomogeneity in the materials for measuring wavelength 1μm is getting poor.

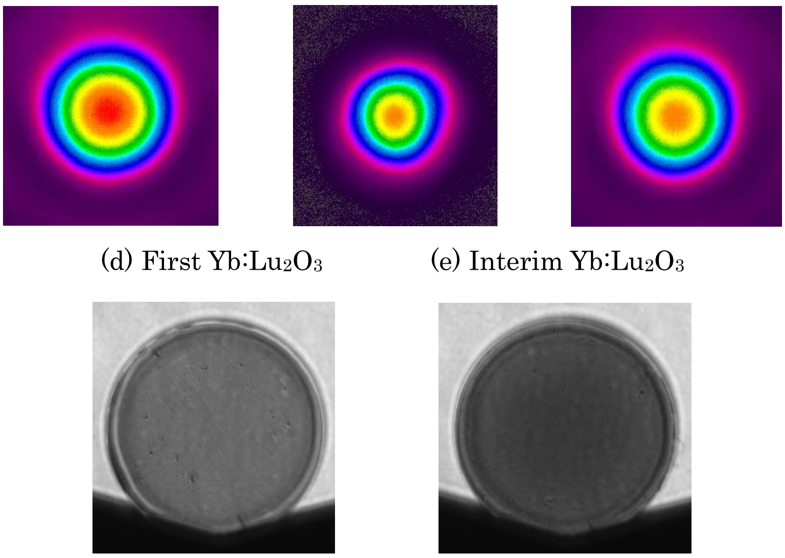


Figure 8 Inspection of optical quality by laser beam profiler (λ=1064nm) and Schlieren imaging system using ND filter.

In the case of Schlieren imaging system, generally white light source (visible light) is used. By using ND filter on the light source, the measuring wavelengths can be collected around only 820nm regions. The results are shown in figure 8d and 8e. In the case of measurement by longer wavelength region, as the light intensity is small and the sensitivity of camera is low, the optical homogeneity in the materials was seemed to be improved compared to the observation by visible light source. This fact is analogous to the results shown in the previous figure 8b and 8c, measurement results done by using longer wavelength laser.

Schlieren images for pure Y_2O_3, 1%Er:Y_2O_3 and 5%Er:Y_2O_3 ceramics are shown in figure 9. Y_2O_3 ceramics without Er doping showed the best optical homogeneity. As the doping amount of Er ions increased, the optical homogeneity was getting worse and worse. This phenomenon was analogous to the previous case of Yb:Lu_2O_3 ceramic materials. It is noted that this technical issue is exceptional to the laser materials related to rare-earth oxides. (In other words, the problem is formation of inhomogeneity in milli~sub milli level caused by doping of laser active ions into the host materials.)

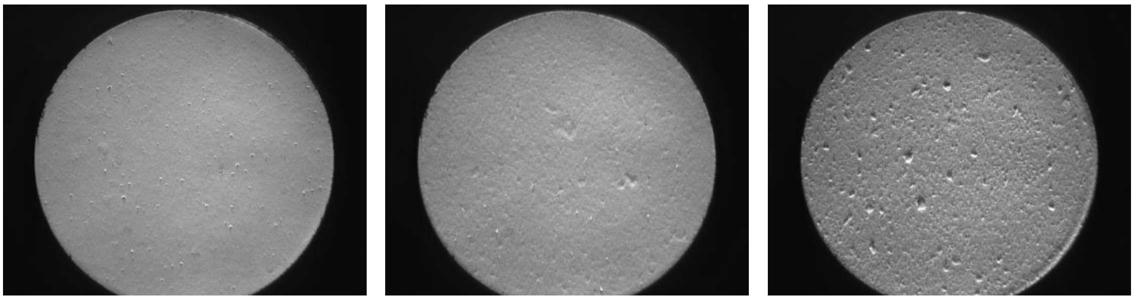


Figure 9 Schlieren images for pure Y_2O_3, 1%Er:Y_2O_3 and 5%Er:Y_2O_3 ceramics (from left to right).

4. Quality analysis by optical and electron microscopy

Reflecting optical microscopy and transmitting optical microscopy for the above mentioned Yb:Y_2O_3 ceramics are shown in figure 10. A homogeneous microstructure with grain size of around a few μm was confirmed. Almost no pores were observed on the surface. From transmitting microscopy, residual pores inside the material were not confirmed but localized inclusions of around several~several tens of μm were observed. By polarized observation, it was detected that the inclusions are cubic crystal system and they have higher refractive index than the host material. Around the inclusions, optical stress due to the mismatch of thermal expansion coefficient between the inclusion and the host material was detected. It is difficult to do chemical analysis as it is located inside the material but it can be estimated from the fabricated composition that the inclusions are more likely to be Yb_2O_3 (rich)-Y_2O_3.

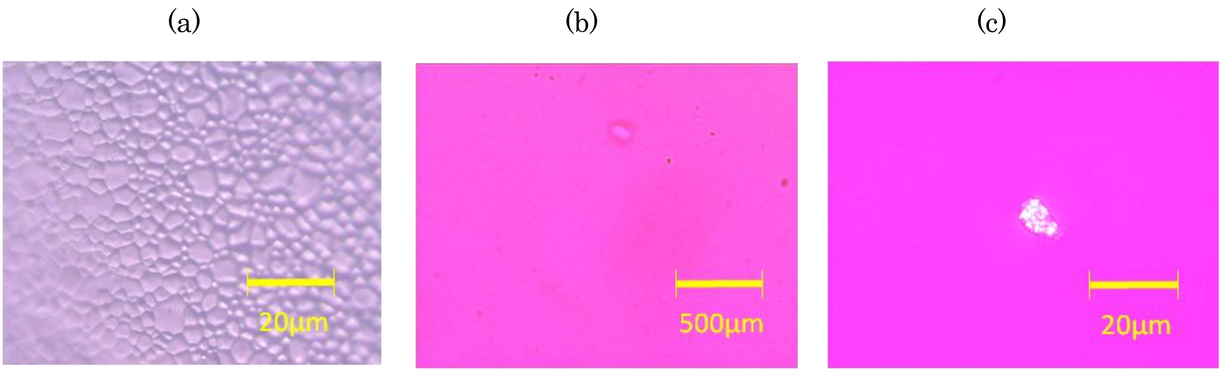


Figure 10(a) Reflecting and (b)(c) transmitting optical microscopy for the $Yb:Y_2O_3$ ceramics.

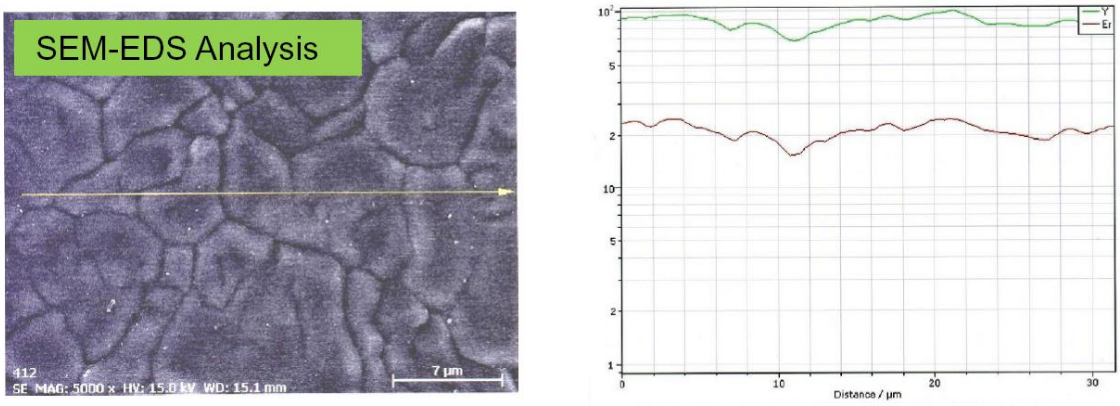
SEM-EDS analysis result for 2%$Er:Y_2O_3$ ceramics is shown in figure 11a. Surface was thermal etched but it was hard to observe the grain boundaries. Line analysis was also done for this sample. Segregation at grain boundary was not recognized. In addition, HRTEM-EDS analysis was also done. These results are summarized in figure 11b. At both low magnification and high magnification observations (lattice structure observation), grain boundary phase was not detected. EDS analysis at inner grain and grain boundary showed that they have similar Er ion concentration, and no other impurity phases were detected.

TEM photograph and EDS analysis result for 1%$Er:Sc_2O_3$ ceramics are shown in figure 12. Even in Sc_2O_3 host material, segregation of Er at grain boundaries and triple points was not detected, and only clean grain boundaries were observed.

Lattice structure and EDS analysis result for $Yb:Lu_2O_3$ ceramics are shown in figure 13. As same as above materials, only clean grain boundaries were observed and segregation of Yb was not recognized.

To summarize the analysis results by electron microscopy, there were no residual pores inside the materials. Their microstructure and chemical composition were found to be homogeneous and only clean boundaries were observed. This means that there are no factors which lower the laser performance of the materials from micron~nano~atomic microstructures.

(a)



(b)

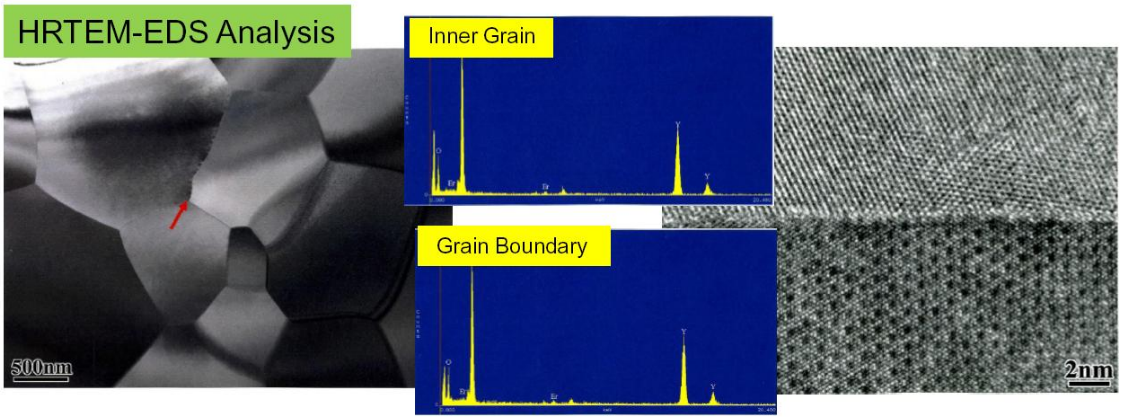


Figure 11(a) SEM-EDS and (b) HRTEM-EDS analysis results for 2%$Er:Y_2O_3$ ceramics.

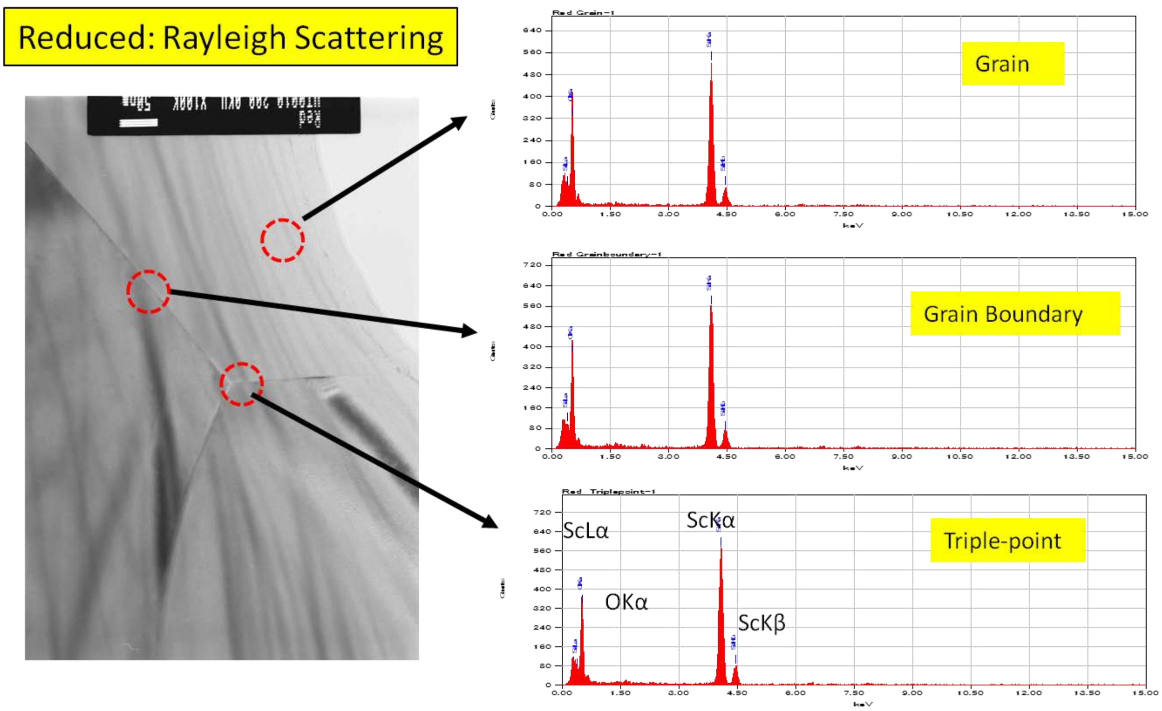


Figure 12 TEM image and EDS analysis of inner grain and grain boundary for 1%$Er:Sc_2O_3$ ceramics.

EDS Analysis Data	Yb(at%)	Lu(at%)
Grain Boundary	6.86	93.14
Inner Grain	6.66	93.34

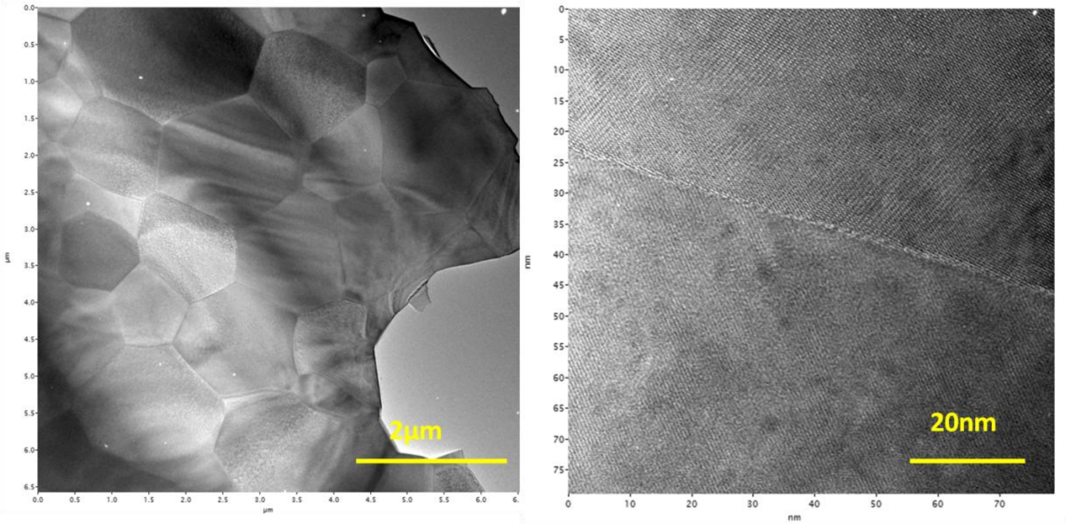


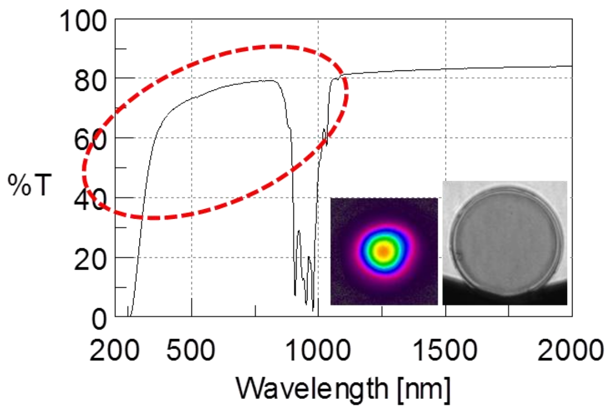
Figure 13 HRTEM observation and EDS analysis of 3%$Yb:Lu_2O_3$ ceramics.

5. Optical properties of ceramics fabricated by using co-precipitated powders

In-line transmittance curves, Schlieren images, and He-Ne laser beam patterns for $Yb:Y_2O_3$ and $Nd:Y_2O_3$ ceramics samples prepared by using co-precipitated powders are summarized in figure 14a. Co-precipitated powders were used in this study because it was estimated that the chemical homogeneity can be kept homogeneous in the end product after final sintering. TEM (transmission electron microscopy) image of 3%$Yb:Y_2O_3$ ceramics prepared by using co-precipitated powder is shown in figure 14b. It was confirmed that the grain sizes of the $Yb:Y_2O_3$ ceramics were around several micron level and it was fully dense. There were no grain boundary phase related to segregation, and clean grain boundaries were observed.

Judging from the measurement results by using optical system such as Schlieren and transmission spectroscopy, and data from microstructure analysis in nano-size by using electron microscopy, there was no improvement related to the optical homogeneity using the co-precipitated powders. It was certain that the chemical composition of the starting powders was homogeneous but unfortunately the sinterability of the co-precipitated powders was reduced, leading to the lowering of in-line transmittance especially in the visible wavelength regions. Simple laser experiments for these samples derived from co-precipitated powders were also done. As there was almost no improvement in oscillation efficiency, these results are omitted in this report. From the current study result, it can be concluded that using co-precipitated powder is not an effective approach. However, if it is possible to produce a co-precipitated powder with good sinterability in the future, the superiority of this approach will be proved.

(a)



(b)

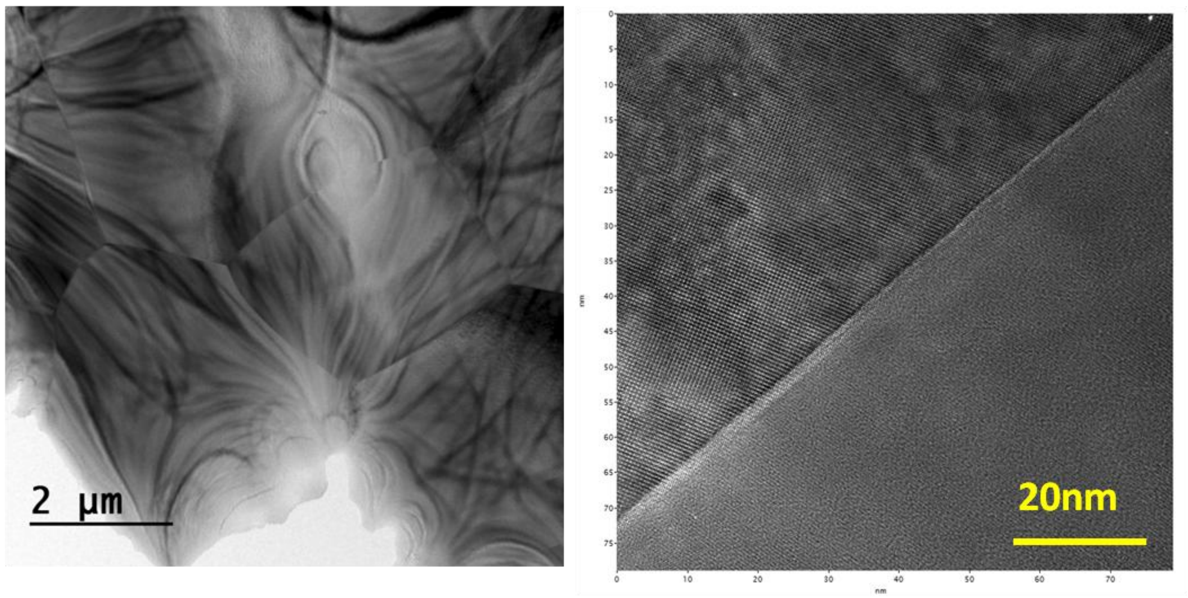
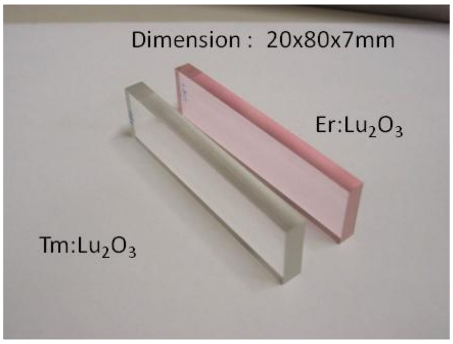


Figure 14(a) In-line transmittance curves, Schlieren images, and He-Ne laser beam patterns for $Yb{:}Y_2O_3$ (left) and $Nd{:}Y_2O_3$ (right) ceramics samples prepared by using co-precipitated powders. (b) HRTEM observation and EDS analysis for 3%$Yb{:}Y_2O_3$ ceramics derived from co-precipitation method

6. Preparation of laser oscillator and laser oscillation experiment

Demonstrated sesquioxide ceramic samples such as $Tm{:}Lu_2O_3$, $Er{:}Lu_2O_3$ (size: 7x20x70mm), and Nd, Yb, or Er doped Y_2O_3 (size: 5x45x100mm) ceramics are shown in figure 15a and 15b, respectively. All ceramics are highly transparent. Undoped Y_2O_3 ceramic disk (without doping of laser active ions) with a large diameter was also demonstrated. A transparent ceramic sample shown in figure 16a has a diameter of 6 inches and 10mm thickness. Its in-line transmittance curve is shown in figure 16b. It was very close to the theoretical transmittance. As it does not include laser active ions, optically heterogeneous parts were not observed in its Schlieren image (see figure 16c).

(a) (b)



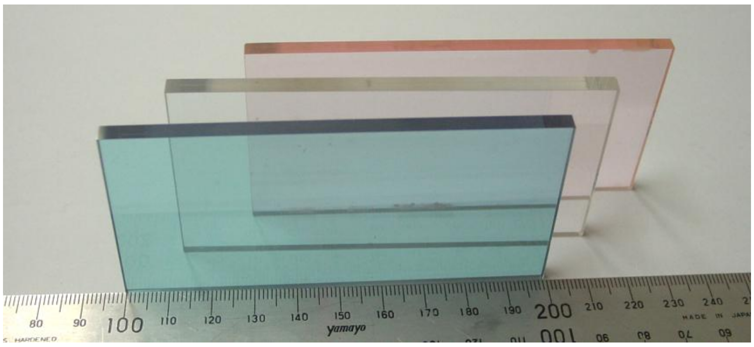
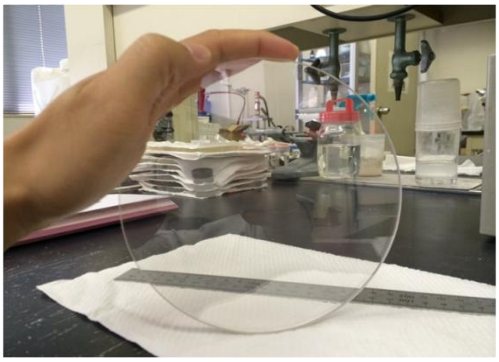
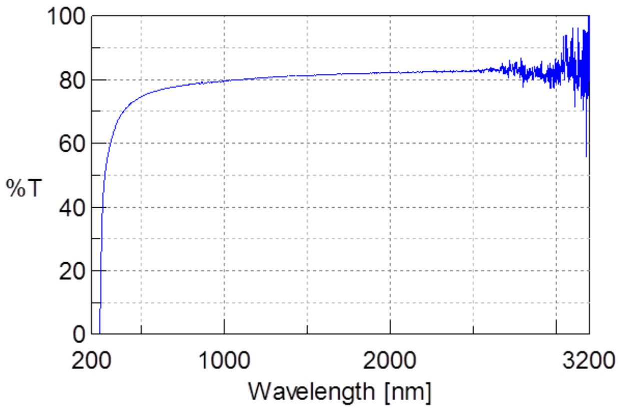


Figure 15 Appearance of demonstrated sesquioxide ceramic samples (a) Tm:Lu_2O_3, Er:Lu_2O_3 (size: 7x20x70mm), and (b) Nd, Yb, or Er doped Y_2O_3 (size: 5x45x100mm) ceramics.

(a) (b)





(c)

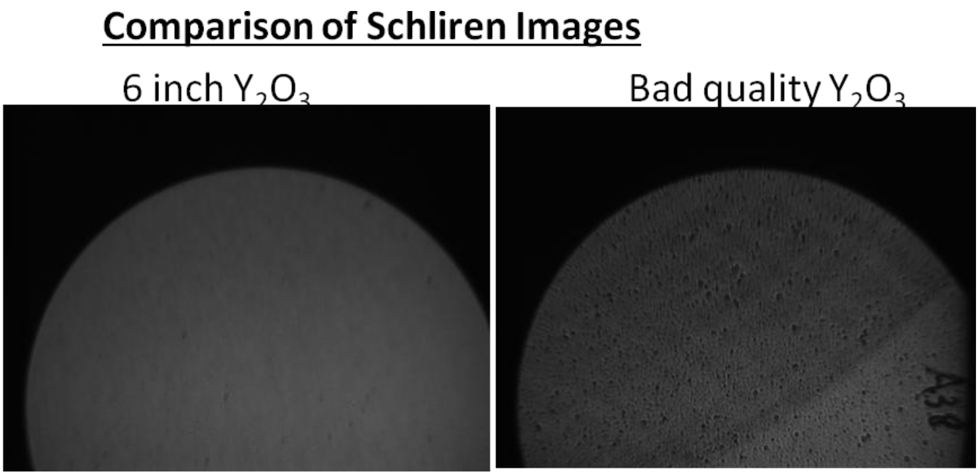


Figure 16(a) Undoped Y_2O_3 ceramic disk, (b) its in-line transmittance curve, and (c) its Schlieren image in comparison with bad quality Y_2O_3 ceramics.

Laser oscillation performance for 1%$Nd:Y_2O_3$ ceramics (Φ9xt10mm) is shown in figure 17a. Lasing wavelength was 1076nm. Output power about 3W was achieved with slope efficiency about 20%. Laser beam quality was very close to Gauss mode. As a reference, figure 17b shows representative inspection results on the optical quality of the 1%$Nd:Y_2O_3$ ceramics (t=5mm) which was used for the above laser experiment. As seen in these results, scattering loss was extremely low, and there were no remarkable inhomogeneity in the materials. The transmitted laser beam pattern was also in good condition but a slightly inhomogeneous domain was observed by transmitted polarized optical microscope.

Laser oscillation performances for 3%$Yb:Y_2O_3$ ceramics are summarized in figure 18. Maximum output power of 5.9W was achieved with slope efficiency of 26%. Due to the limitation of LD (laser diode) pumping power, it was difficult to increase the output power. When the thickness of this ceramic material was reduced to 2mm, slope efficiency was improved to nearly 40% but in the case of sample with a laser gain length (thickness) of 30mm, slope efficiency remarkably decreased to 3~5% only. It was recognized that the laser oscillation efficiency of rare-earth oxide ceramics is closely related with the length of laser gain media. But the true nature of the problem may be directly related to the inhomogeneity of the materials that was found in the above inspections. As the laser gain length gets longer, a probability of laser beam to collide with the optically inhomogeneous parts gets higher and higher, leading to lowering of laser oscillation efficiency. In the literatures about the rare-earth oxide materials up to now, basic properties of laser such as ①oscillation efficiency, ② output power, and ③beam quality etc. are inferior to that of the existing garnet materials. In most of the papers, it can be noted that the gain length of the materials was smaller than about 1~2mm (volume of gain media: $<2 \times 10^{-2} cm^3$). [1, 2] In the case of longer gain length (or larger volume), satisfactory results were hardly obtained. [3] For laser oscillators with powerful cooling system (e.g., cryostat condition) or laser setup with LD pumping system, required size and demanded optical quality for laser gain media can be somewhat mitigated.

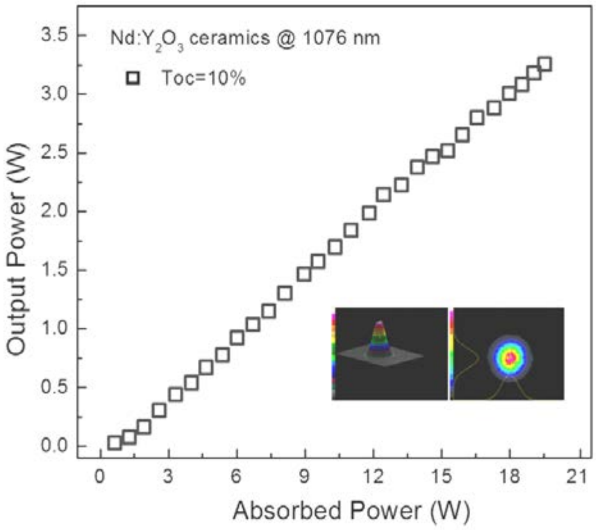
We can estimate that application to a thin disk laser will be an effective approach to extract good laser performance using this ceramic material. However, it will take about one year for polishing, coating and bonding of thin disk to heat-sink etc. As our collaborator (laser scientist) has no experience on thin disk laser, we gave up the laser oscillation using thin disk laser approach.

Apart from this project, we have produced 3%$Yb:Lu_2O_3$ ceramics for our domestic client. It was processed into thin disk shape with a thickness of 0.2mm. They have achieved laser generation from the thin disk with an output power over 100W and slope efficiency over 50%. [4] Among the reported literatures related to rare-earth oxide lasers up to now, it is not too much to say that this result is the highest level.

As mentioned above, the main issue of this type of ceramic materials is a slight fluctuation of refractive index throughout the materials. Therefore, the only thing that can be said with certainty is that thin disk laser operation is the most effective approach to extract the best performance of the current laser materials because thin disk shape is less affected by the fluctuation of refractive index.

However, development of laser gain media with homogeneous refractive index distribution is very important for high energy laser applications because large scaled laser gain media are essential for generation of high energy laser.

(a)



(b)

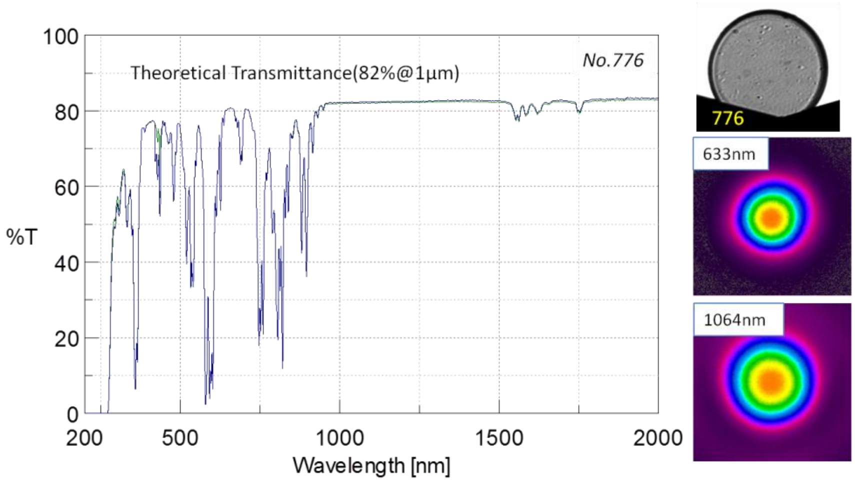


Figure 17(a) Laser oscillation performance for 1%Nd:Y_2O_3 ceramics (Φ9xt10mm). (b) In-line transmittance, Schlieren image and inspection with beam profiler for the Nd:Y_2O_3 ceramics.

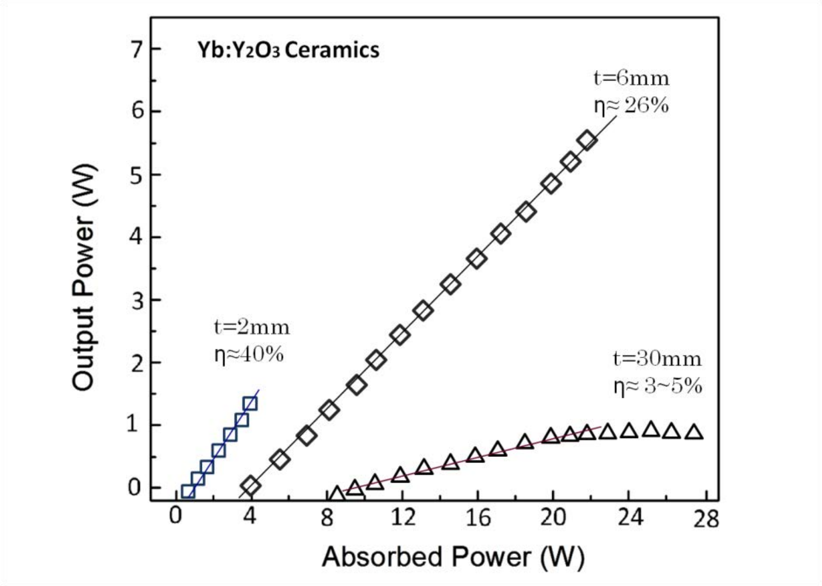


Figure 18 Laser oscillation performances for 3%Yb:Y_2O_3 ceramics.

7. Conclusions

In the literatures about rare-earth oxide lasers reported up to now, there were almost no discussions on correlation between material process⇔optical property⇒laser performance but the discussions were only focused on laser oscillation efficiency. In most of the technical papers, thin disk operation scheme was applied, and as a result, the benefits of the laser system were being reflected. Of course, thin disk laser is a useful technology to generate high power laser but it is necessary to improve the realistic technical issues of the sesquioxide ceramics from a standpoint of material development in order to provide high quality materials.

The following results were obtained from this project.

1) Fabrication of highly transparent (theoretical transmittance) rare-earth oxide ceramics was successful.

2) In-line transmittance and optical homogeneity of host materials such as Sc_2O_3, Lu_2O_3 and Y_2O_3 ceramics were excellent.

3) Optical homogeneity was lowered by adding laser active ions into the above host materials.

4) Optical heterogeneity was caused by the inhomogeneous distribution of laser active ions in the host materials.

5) Due to the phenomenon described in 4), laser oscillation efficiency gets lower or in the worst case, laser oscillation is not possible. (However, when the laser gain length is extremely reduced, both laser output power and laser oscillation efficiency can be significantly improved.)

6) Even for ceramic materials derived from co-precipitated powders, improved performance was not recognized (as of this current project).

7) Production of large scaled laser gain media by ceramic process is available.

The outstanding issue is the formation of optically inhomogeneous parts when laser ions are doped into the host materials. The following investigations are required to resolve the above mentioned technical issue.

1) Development of chemically homogeneous co-precipitated powders with good sinterability and optimization of sintering process for those starting materials.

2) Development of mixing process in solid-state method that can provide homogeneous dispersion of laser active ions in the host materials and optimization of sintering process for those starting materials.

In conclusion, "whether the development of laser materials is successful or not" is finally reflected by the laser oscillation results but before that, verification on material science is more important.

References

[1] M. Tokurakawa, A. Shirakawa, K. Ueda, H. Yagi, M. Noriyuki, T. Yanagitani, A. Kaminskii, "Diode-pumped Ultrashort-pulse Generation based on Yb^{3+}:Sc_2O_3 and Yb^{3+}:Y_2O_3 Ceramic-gain-media Oscillator", Opts. Expr., 17, 3353-3361 (2009).

[2] J. Sanghera, J. Frantz, W. Kim, G. Villalobos, C. Baker, B. Shaw, M. Hunt, F. Miklos, A. Lutz, I. Aggarwal, "10%Yb^{3+}:Lu_2O_3 Ceramic Laser with 74% Efficiency", Opt. Lett., 36, 576-578 (2011).

[3] L. Wang, H. Huang, D. Shen, J. Zhang, H. Chen, Y. Wang, X. Liu, D. Tang, "Room Temperature Continuous-wave Laser Performance of LD Pumped Er:Lu_2O_3 and Er:Y_2O_3 Ceramic at 2.7μm ", Opt. Expr., 22 [16] 19495-503 (2014).

[4] Unpublished work (to be submitted in near future)